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(54) Method for the production of cold rolled steel sheet having super deep drawability.

(57) The subject matter of the invention is a method for the production of a cold rolled steel sheet which has a distinguished deep drawability as well as chemical treating ability by the steps of providing a very low carbon steel, adding Ti and Nb in combination to said steel, hot rolling and cold rolling said steel to produce a cold rolled steel sheet, and subjecting said cold rolled steel sheet to a continuous anneal at a temperature of more than 700°C to less than the Ac<sub>3</sub> transformation point. The steel may also contain less than 30 ppm B.

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METHOD FOR THE PRODUCTION OF COLD ROLLED  
STEEL SHEET HAVING SUPER DEEP DRAWABILITY

The present invention relates to a method for producing a steel sheet having super deep drawability, more particularly, to a method for producing a cold rolled steel sheet having excellent secondary workability as well as good chemical treatability.

There are two general categories of steel sheet having super deep drawability: Ti killed steel sheet such as that described in Japanese published examined patent application No. SHO44(1969)-18066 and Nb killed steel sheet such as that described in US Patent 3,522,110.

In this connection, as it has become easily possible to reduce the C content of Nb killed steel to the level of  $C < 50$  ppm, there have been recent reports in the literature of the feasibility of producing Nb killed steel sheet with low C and Nb contents. On the presumption that the steel sheet is to have a very low C content, Ti or Nb, both of which have a strong tendency to form carbide and nitride, is added to obtain steel sheet containing almost no interstitial elements such as C or N. There is thus the advantage that a steel sheet product of about the same quality can be obtained using either continuous or box annealing. In the case where the steel sheet is produced using the continuous anneal, however, there is encountered certain disadvantages as discussed

in the following.

In the case of Ti killed steel, there is the disadvantage that secondary work cracking tends to occur. In particular, when, with the aim of obtaining a high quality steel, Ti is added to the steel at more than  
5 an equivalent amount with respect to C or N, an increase in the P content will increase the risk of the secondary work cracking. Further, there is a disadvantage that addition of P will degrade the r value.

10 In addition, in the production of a steel sheet coated with alloyed zinc by means of the Sendzimir continuous molten zinc coating process, which constitutes one type of continuous annealing, the alloying proceeds so excessively that the coating becomes easy to peel off  
15 (this phenomenon is termed, "powdering" hereinafter) when the sheet is subjected to the press forming work. On the other hand, there is the advantage that a steel sheet of stable quality can be produced using continuous anneal even at an ordinary coiling temperature of 600 -  
20 650°C.

In contrast, in the case of Nb killed steel, it is necessary to coil the hot rolled strip at a high temperature (coiling temperature  $\geq 700^{\circ}\text{C}$ ). This is because when coiling is carried out at an ordinary coiling  
25 temperature, the complete recrystallization temperature becomes so high that a semi-recrystallized portion remains when annealing is carried out within the

temperature range feasible with a continuous annealing oven (not more than about 850°C) and, moreover, because in such case the quality varies greatly with the amount of Nb. It has frequently been reported that when coil-

5 ing is carried out at a high temperature, it is possible to obtain a steel sheet having a high r value in all but the end portions of the hot rolled strip at an annealing temperature of about 800 - 850°C. In the high temperature coiling, however, the formed scale becomes so thick

10 as to impair the pickling efficiency. Moreover, as the rate of cooling at the coil ends is high, it becomes impossible to obtain a product of sufficient quality. For these reasons, there is a pronounced decline in product yield.

15 A very low carbon steel sheet added with Ti and Nb is disclosed in U.S. Patent No.3,765,874. The amount of Nb is more than 0.025%, and a steel sheet containing more than 0.025% Nb as a solid solution is disclosed in the above patent.

20 The inventors have investigated the steel of the above composition in detail, and found that this steel sheet has the following defects.

As the recrystallization temperature is considerably high, a good quality cannot be obtained by the

25 usual anneal temperature. In the rapid heating and short time annealing, such as continuous anneal, and in the feasible annealing temperature (usually, less than

850°C), a satisfactory recrystallization will not take place, or the grain growth after recrystallization never occurs.

5 The addition of too much Nb has the following effects: (1) Carbide thus precipitated is fine, so the migration of the grain boundary is greatly hindered by the precipitate; (2) the growth of recrystallized grain is considerably restricted by the solution drag effect due to the high content of Nb in solid solution. In other words, since Nb is too  
10 much, as described hereinbefore, it has the same defect as that of the Nb killed steel.

In the steel stock for the continuous anneal, a good  $r$  value and  $E\ell$  cannot be obtained by the low temperature coiling, and the stock is hard; the deterioration of  
15 quality of the coil end portion is still remarkable even after high temperature coiling. And furthermore, as the steel contains too much of both Ti and Nb, it is needless to say that its chemical treatability is inferior.

20 It is a prime object of the present invention to provide a method for producing a cold rolled steel sheet having excellent ductility as well as deep drawability by adding Ti and Nb in combination to a very low carbon steel.

25 It is another object of the invention to provide a method for producing an excellent cold rolled steel sheet having a uniform mechanical property in the longitudinal direction of the coil and exceedingly small

anisotropy of the  $r$  value by adding Ti and Nb in combination to a very low carbon steel.

It is still an additional object of the invention to provide a cold rolled steel sheet having outstanding  
5 chemical treatability by adding Ti and Nb in combination to a very low carbon steel.

Other and further objects of the invention will become apparent to those skilled in the art from the  
10 following detailed description of the invention with reference to the drawings, in which:

Fig. 1 is a graphic view explaining the effect of Ti content on the characteristics of a steel to which both Ti and Nb have been added;

15 Fig. 2 is a graphic view explaining the effect of Nb content on the characteristics of a steel to which both Ti and Nb have been added;

Fig. 3 is a graphic view explaining an annealing cycle;

20 Fig. 4 is a graphic view explaining the distribution of a test value of the quality in the longitudinal direction of the coil;

Fig. 5 is a graphic view explaining the temperature zone in which secondary work cracking takes place;

25 Fig. 6 is a graphic view explaining the  $r$  value and the anisotropy of the  $r$  value;

Fig. 7 is a graphic view explaining the dependence

of the r value on the reduction during cold rolling;

Fig. 8 is a graphic view explaining the distribution of test values of quality in the longitudinal direction of the coil; and

5 Fig. 9 is a graphic view explaining the annealing cycle.

The inventors conducted an extensive and detailed research on the merits and demerits of Ti killed and Nb  
10 killed steels. Their conclusions regarding the behaviors of these steels are outlined in the following. Ti being a very powerful nitride forming element, TiN is found to be already formed in the heating furnace before hot rolling. Although the precipitation temperature of  
15 carbides is lower than that of nitrides, it is considered that a considerable portion of the carbides precipitate and a nitride turns in a nucleation site while the steel strip is being coiled at a temperature of 600° - 650°C. Accordingly, a considerable part of the precipitation  
20 takes place even at a low coiling temperature so that coarse precipitates are present in the hot coil. Therefore only little precipitation takes place during continuous annealing after the cold rolling. Thus, it is considered that the recrystallization temperature will  
25 not become exceptionally high and that the product quality will be fairly uniform.

Because of this almost complete precipitation of C

and N, the grain boundary becomes clean and this promotes the segregation of such impurity elements as P. As a result, the grain boundary is embrittled and secondary work cracking occurs.

5 In addition, in the production of a Ti killed steel sheet coated with the alloyed zinc, it is thought that the powdering phenomenon tends to occur because the alloying reaction between the iron base and molten zinc is promoted to the extent that over-alloying occurs.

.0 On the contrary, however, Nb is considerably inferior to Ti in its ability to form nitride. As a matter of fact, in the steel containing Nb, although Nb forms carbide, N precipitates as AlN. AlN is hardly formed in low temperature coiling and it is not formed  
5 in the hot rolled steel sheet unless the coiling temperature is raised to more than 700°C; and it precipitates in a fine form during continuous annealing after the cold rolling, which results in quality deterioration owing to increased yield strength and degraded elongation  
10 property and r value. Accordingly, even if coiling is carried out at a high temperature, the quality of the end portions of the hot rolled steel becomes no better than that obtained with low temperature coiling because the cooling rate of these portions is high.

5 Besides, it is considered that the deterioration of quality in the leading and trailing end portions of the hot rolled coil and the fluctuation of quality throughout



the coil result from the difference in the degree of forming of AlN at the center and end portions of the coil and also from slight fluctuations in the coiling temperature of the hot rolled strip. However, as Nb has less carbonitride forming power than Ti, several ppm of carbon is so segregated in the grain boundary that the bond energy at the grain boundary is much increased with the result that there is no fear of secondary work cracking in spite of the considerably high content of P. Further, in the production of an alloyed zinc coated steel sheet, since Nb does not promote the alloying reaction between the iron base and the molten zinc as much as Ti, powdering is less apt to occur in an Nb killed steel than in a Ti killed steel.

Based on the above findings, the inventors proceeded to develop a method for the production of a super deep drawable steel sheet which has good homogeneous quality throughout the coil, is free from the risk of secondary work cracking, and, in the production of an alloyed zinc coated steel sheet is free from powdering. The fundamental principle employed in this invention to realize such a steel sheet is to cause N to precipitate in the steel sheet not as AlN but as TiN by the action of Ti before the finish hot rolling step, and to cause C to precipitate as a combined carbide such as (Ti·Nb)C.

As fully described hereinafter, the steel of this invention is superior to Ti killed steel in that the r

value is not degraded when the strength of the steel is increased by the addition of P and in that almost no secondary work cracking takes place. Further, the steel of this invention is also advantageous in that almost  
5 no powdering occurs in the production of an alloyed zinc coated steel sheet.

In accordance with this invention, differently from the case of Nb killed steel, N is fixed as TiN, not as AlN, whereby nearly the same product quality can be  
10 obtained using low temperature coiling as that obtained by carrying out high temperature coiling and whereby the steel of this invention is made superior to any steel of prior art in respect of its exceedingly homogeneous quality in both the longitudinal and width directions  
15 of the steel coil. These advantages of the steel according to this invention provide it with various excellent properties not possessed by either Ti or Nb killed steel. The invention thus has great merit.

In addition, the steel of the invention to which Ti and Nb are added in combination has a unique property  
20 not inferable from either Ti or Nb killed steel of the prior art, namely it has very small anisotropy of the r value. In general, the r value of Ti or Nb killed steel is the worst in the rolling direction (L direction) or  
25 in the direction at 45° thereto while it is best in the direction at 90° to the rolling direction (C direction). However, the r value of the steel of the invention is

almost the same in the L, C and 45° directions, or it is somewhat large in the 45° direction, and this property of the steel is maintained regardless of the amount of cold rolling reduction.

5           Never before has there been known a high r value steel sheet with such a low anisotropy.           The steel thus is not only very interesting from the scientific aspect but also has considerable advantages from the commercial point of view. Particularly, it can be expected to exhibit outstandingly good formability in the case of drawing a square cylindrical body (with 45° corners). The steel can be expected to be advantageously applied even to deep drawing of circular cylinders, a process in which the rupture limit is frequently  
10 determined by the least r value. Furthermore, minimum anisotropy is very advantageous in, for instance, the drawing of the outer cylindrical case of a dry cell where the uniformity of the sheet thickness after deep drawing is critical, and in other uses where the formation of ears must be avoided as much as possible.  
15

20 Accordingly, the steel sheet of the present invention can be expected to attract wide interest not merely from the point of the average of the r value in three directions but from the point of its extremely low anisotropy.

25           The steel of this invention is superior in every respect to steels containing Ti or Nb only and constitutes an entirely new and novel steel having a totally

unexpected property.

The chemical composition of the steel according to this invention will now be defined in weight %.

As mentioned above the amount of Ti to be added depends on the amount of N. AlN, as described hereinbefore, is one of the causes to deteriorate the quality of end portions of the coil which is coiled at high temperatures and the quality of total portions of the coil which is coiled at low temperatures. Therefore, from the viewpoint of quality, the amount of N which is precipitated as AlN is required to be limited to at most

20 ppm. From this respect, the lower limit of the content of Ti should be 48/14 (N% - 0.002%), as follows:

$$Ti > \frac{48}{14} [N\% - 0.002\% (20 \text{ ppm})]$$

If Ti is added in more than the equivalent amount (of the resultant steel) of C+N, the property resembles that of the Ti killed steel mentioned hereinbefore; namely, the second workability is deteriorated, and the values of El and r are deteriorated when P is added. In addition, when the alloyed zinc coated steel sheet is produced, there arises a distinct defect that powdering tends to occur. Therefore, it would not satisfy the object of the present invention. Accordingly, Ti should be added less than the equivalent amount of C+N. Hence it follows:

$$Ti\% < (48/12C\% + 48/14N\%)$$

From the economical viewpoint, the increase of the amount of Ti is not preferred, and the most desirable amount of Ti is less than the equivalent of N, namely,  $Ti\% \leq 48/14N\%$ .

5           On the other hand, the amount of Nb depends on C. More specifically, Nb should be added at the rate of 0.3 times as much as the amount of C in terms of atomic ratio, as follows:

10                           
$$Nb\% > 0.3 \times 93/12C\% = 2.33C\%$$

Moreover, Nb should be added in an amount of not less than 0.003% to less than 0.025%. In the range of  $Nb\%/C\% < 2.33$  and  $Nb < 0.003\%$ , a combined carbide  $(Ti \cdot Nb)C$  is not formed and a solid solution C remains, and this  
15 gives rise to the problem that a non-ageing steel is not obtained. And in the range of  $Nb \geq 0.025\%$ , the properties of the steel resemble those of the Nb killed steel, its recrystallization temperature increases, and quality deterioration in the leading and trailing end  
20 portions of the coil also increases. Such a steel departs from the principle of the present invention.

Figs. 1 and 2 show the range of the steel of this invention in terms of the amount of Ti and Nb.

Fig. 1 is a graph showing how the properties of the  
25 steel change when the amount of Nb is fixed (at 0.022%) and the amount of Ti is varied. The sample steel contained 0.005%C, 0.01%Si, 0.25%Mn, 0.02%P, 0.01%S, 0.06%sol.Al

and 0.005%N and was coiled at 720°C in the hot rolling step. In Fig. 1, "a" refers to the center of the coil in the longitudinal direction and "b" to the leading and trailing end portion of the coil.

5 In case the amount of Ti is insufficient relative to the fixed amount of N, namely,  $48/14(N\% - 0.002\%) > Ti$ , the quality deterioration of the leading and trailing end portions of the steel coil is particularly great. Besides, the anisotropy of the r value resembles that  
10 of a very low carbon steel added with a very small amount of Nb, and the effect of adding Ti and Nb in combination is small.

On the contrary, however, in case Ti is added in more than an equivalent amount relative to C and N, it  
15 is seen that the deterioration of quality in the leading and trailing end portions of the coil is considerably small while, on the other hand, the anisotropy of the r value is similar to that of Ti killed steel. In other words, it is only when 0.010 - 0.037%Ti is added that the  
20 effect of improving the texture of steel sheet due to the addition of Ti and Nb in combination appears and it is only within this range that there is obtained an excellent r value with a very small anisotropy.

In order to attain the excellent isotropy of the r  
25 value, the addition of Ti and Nb in combination is absolutely indispensable. This property is due to the texture of steel sheet which cannot be obtained by the

addition of either Ti or Nb only.

Fig. 2 is a graph showing how the properties of the steel change when a certain amount (0.02%) of Ti sufficient to fix N is added while the amount of Nb added is varied. The chemical composition of the sample steel was nearly the same as that of Fig. 1. Similarly to what was seen in connection with Fig. 1, when the amount of Nb is low (less than 0.011%) relative to the amount of C, the characteristics are similar to those of a very low carbon steel, namely the  $r$  value in the  $45^\circ$  direction is very low while the anisotropy is high. Also similar to the case of Fig. 1, the deterioration of quality in the leading and trailing end portions of the coil is large, and the non-ageing property is not obtained. If the amount of Nb exceeds 0.025%, the anisotropy of the  $r$  value assumes the same tendency, but there appears a disadvantage that the  $r$  value in the C direction decreases, and the deterioration of quality in the leading and trailing end portions of the coil is very great. These disadvantages are similar to those peculiar to Nb killed steel.

As clearly shown in Fig. 2, addition of Ti and Nb together makes the anisotropy of the  $r$  value small and, further, makes it possible to realize uniform quality of the coil in its longitudinal direction. These characteristics cannot be attained by the addition of either Ti or Nb only to the steel, indicating that the addition

of Ti and Nb in combination is indispensable.

The reason why a high quality can be more stably obtained independently of the coiling temperature than in the case of the addition of Nb only, and further, the reason why a high quality can be obtained by the addition of a smaller amount of an alloying element than in the case of the addition of Ti only is presumed to be explained as follows: when the steel contains Ti and Nb together in a well-balanced ratio in accordance with the method of the present invention, a combined precipitate (Ti·Nb)C is formed, and this precipitate has a high start temperature of precipitation as compared with TiC and NbC, with the result that coarse precipitates are formed. Thus, it is presumed that a favorable recrystallization behavior is observed despite the low coiling temperature and this appears to be the reason for the isotropic r value obtained. On the contrary, however, in a steel containing Nb only or Nb  $\geq$  0.025%, it is NbC which forms, and the precipitation condition greatly varies with the coiling temperature. In case of a low temperature coiling, the steel quality is greatly deteriorated because fine NbC precipitates raise the recrystallization temperature at the time of continuous annealing. Besides, in the addition of Ti only, the steel quality is also greatly deteriorated unless the atomic ratio of Ti to C+N is more than 1. It appears that the steel becomes hard and the ductility is deteriorated because TiC is not



fully precipitated in the hot rolled steel sheet, but is finely precipitated at the time of the continuous annealing unless the amount of Ti is much increased.

As fully described in the foregoing, in accordance with this invention a steel having excellent ductility as well as excellent deep drawability can be obtained by the addition of Nb and Ti in combination, particularly, by the addition of 0.003 - 0.025%Nb.

As described above, the composition range of the steel of the invention is as follows: the amount of Ti to be added depends on the content of N of the steel, and Ti should be contained in a sufficient amount so as to satisfy the following relation:

$$\text{Ti}\% > 48/14(\text{N}\% - 0.002\%)$$

and

$$\text{Ti}\% < (48/12\text{C}\% + 48/14\text{N}\%)$$

The amount of Nb to be added depends on the carbon content of the steel, and Nb should be also contained in a sufficient amount to satisfy the following relation:

$$\text{Nb}\% > 0.3 \times 93/12\text{C} = 2.33\text{C}\%$$

and

$$0.003\% \leq \text{Nb}\% < 0.025\%$$

The total amount of Nb and Ti should, however, be subject to the following limitation from the point of the steel's chemical treatability.

The chemical treatability of a steel sheet (how well it is adapted to phosphating) depends on the steel surface condition. In the case of an outer panel sheet of an automobile, for example, the sheet may be formed, assembled and locally machined with a grinder so that its interior is exposed. In such case, the steel sheet itself should have good chemical treatability. However, a very low carbon steel containing Ti and/or Nb is so deficient in chemical treatability that the phosphate film locally fails to form.

The inventors have found that it is necessary for forming a uniform coating of phosphate film over the steel sheet to restrict the amount of Ti plus Nb to less than 0.04%.

It is because a tenacious oxide film tends to easily form on the surface of the steel sheet with the increase of the amount of Ti and Nb; the tenacious oxide film is hardly reduced, and has a low reactivity with the acid. Furthermore, the matrix of the steel sheet is so purified that the reaction with the Bonderite solution is deteriorated. By carrying out the production process under the above condition, the phosphate treating ability is satisfactory; particularly, when treated in accordance with

$$0.01\% < \text{Ti}(\%) + \text{Nb}(\%) < 0.04\%$$

the treating ability is most excellent.

In case the amount of Ti and Nb to be added is exceedingly small (the whole amount is less than 0.01 %), the amount of precipitate (carbide and nitride) to be formed is little, hence the location where there is any difference of surface energy on the surface of the steel sheet, namely, the location where the reaction with the Bonderite solution is active is decreased.

The chemical components of such a sheet other than Ti and Nb are: less than 0.007%C, less than 0.8%Si, less than 1.0%Mn, less than 0.1%P, 0.01 - 0.1%Al, less than 80 ppm N, and other unavoidable impurities.

If the C content is too high, much Nb is required to fix C and the amount of (Ti-Nb)C increases so much that it prevents the growth of recrystallized grains, which results in deterioration of the r value, a rise in yield strength, and a decrease in elongation property. Therefore C should be less than 0.007% from the viewpoint of producing the super deep drawable steel sheet.

In the production of a molten zinc coated steel sheet, Si has a tendency to lower the adherence of the coating layer, so it is preferred to be less than 0.8%. Particularly, in case the alloying treatment is not carried out, Si is preferred to be less than 0.3%.

If much Mn is added, the r value is very much deteriorated. Hence, the upper limit for Mn is set at 1.0%, and the lower limit of Mn is desired from the viewpoint of obtaining a high r value.

In the steel of this invention, almost no secondary work cracking takes place due to the addition of Ti and Nb together. But if the steel contains much P, the amount of P segregated on the grain boundary increases so much that the grain boundary is embrittled to promote secondary work cracking. Hence the upper limit of P is 0.1%.

In order to suppress the secondary work embrittlement, it is effective to add B, and the amount of B to be added is preferred to be less than 30 ppm. In addition, the inventors have found that the ageing property is not deteriorated, but baked hardenability is enhanced by adding a very little amount of B. In the steel containing Nb only, B combines with N to precipitate BN, hence it is required to add B in an amount of more than the equivalent relative to N. In order to attain the effectiveness of B so that the amount of B to be added is inevitably increased. Besides, in the steel containing Ti only, the purification of the steel is considerably high, so it is not effective to add very little B; while B forms no BN, it is inevitable to add much B. Therefore in the steel containing either Nb or Ti alone, the secondary work embrittlement can be controlled by adding more than several 10 ppm B.

On the other hand, B in the steel, whether it may form BN or solid solution B, considerably tends to deteriorate the yield strength (YS), ductility (EL), and deep

drawability (r value) or also tends to increase the recrystallization temperature. Therefore the amount of B to be added is preferred to be as small as possible. Since the present invention is directed to fix N with a very  
5 small amount of Ti, so the addition of a very small amount of B (less than 30 ppm) is effective to attain the effect already mentioned. Accordingly, as compared with the steel of prior art, the steel of the invention has a distinguished good property (YP, El and r value),  
10 low recrystallization temperature, eminent secondary workability, and enhanced effect of bake hardenability. Without having an undesired effect on mechanical quality and ageing, the addition of B in an amount of more than 2 ppm to 10 ppm is preferred so as to attain the perfec-  
15 tion of the secondary workability and enhancement of bake hardenability.

Al is added to the molten steel as a deoxidizer prior to the addition of Ti and Nb. If the amount of Al is too small, the deoxidizing action is not fully carried  
20 out and instead, Ti and Nb act as deoxidizers, in which case the reduction in the yield of Ti and Nb becomes pronounced. Conversely, if too much Al is added, the amount of  $Al_2O_3$  inclusion increases undesirably. Based on the above reason, Al should be in the range of 0.01 -  
25 0.1%.

N is fixed in the form of TiN by Ti, but if N is too much, the required amount of Ti increases undesirably.

Therefore N should be less than 80 ppm.

Now, the condition for the production is described. In this invention, the usual hot rolling condition will do. With reference to the influence of the coiling temperature, owing to the reason already mentioned, as compared with the steel added with Nb only, a good quality can be obtained by the usual coiling temperature. Particularly, in order to attain the uniform quality throughout the whole length of the coil, the low temperature finish and low temperature coiling are extremely effective. In accordance with the invention, as already mentioned, with the addition of Ti and Nb together, TiN precipitates in the heating furnace for hot rolling, and further, such a composite precipitate as (Ti-Nb)C precipitates sparsely at the time of finish hot rolling, hence an excellent quality can be obtained even at a rather low temperature of coiling. However, in order to make the above-mentioned precipitates at the finish hot rolling in a full and satisfactory manner, it is effective for the finish temperature to select a low temperature less than  $Ar_3$  point, in other words, the finish temperature is preferred in the range of more than  $720^{\circ}\text{C}$  to less than  $870^{\circ}\text{C}$ . If the finish temperature is lower than  $720^{\circ}\text{C}$ , the Goss orientation is so developed to reduce the r value. If the coiling temperature is also more than  $680^{\circ}\text{C}$ , the grains in the hot rolled strip turn to be coarse to reduce r value. The uniform quality throughout

the whole length of the coil becomes extremely excellent by the low temperature finish hot rolling.

As compared with a steel hot rolled by the high temperature finish hot rolling, the steel of the invention has a merit, such as, a relatively high r value even with a low rate, 60 - 75% of cold rolling.

If the above low temperature finish hot rolling process includes the limitation of the heating temperature of a steel slab, a much stabler and better quality of the steel can be obtained. The range of heating temperature is more than 950°C to less than 1170°C. In this range of temperature, a nucleus of precipitate (Ti-Nb)C already forms in the heating furnace, hence it is effective. At a heating temperature of more than 1170°C, the precipitation of (Ti-Nb)C delays and it becomes so fine that the steel sheet is hardened; hence its ductility is deteriorated, and at a heating temperature of less than 950°C, the results of the steel at the above finish temperature is hardly obtained.

As regards the descale treatment and cold rolling condition, it is not particularly required to specify them definitely. However, from the viewpoint of attaining a high r value, a rate of cold rolling of more than 60% is desirable. With reference to the recrystallization anneal, in view of secondary workability, productivity, and uniform quality in the longitudinal direction of the coil, it is not a box anneal, but an anneal process of

the continuous type wherein the rapid heating, short  
time annealing, and quick cooling are possible, which is  
preferred in order

to control the diffusion of such an element as P and  
the like which embrittles the grain boundary in con-  
nection with the secondary workability. The anneal  
temperature should be adopted in the range of more than  
the recrystallization temperature to less than  $A_{c3}$  point.  
The cooling cycle after the anneal is not particularly  
required to specify, but the usual continuous annealing  
cycle will do.

Now, the examples of the present invention will be  
described hereinbelow.

Example 1

Table 1 shows the chemical composition of the steel  
of the invention together with those of other steel  
samples for comparison.



Table 1

Sample Steel No.	Chemical Composition (wt%)										Remarks
	C	Si	Mn	P	S	sol.Al	N	Ti	Nb	$\frac{Nb}{C}$	
1	0.004	0.010	0.15	0.015	0.008	0.042	0.0042	0.012	0.020	5.0	The invention
2	0.006	0.021	0.14	0.011	0.009	0.048	0.0057	0.021	0.015	2.5	"
3	0.004	0.019	0.30	0.020	0.005	0.051	0.0064	0.022	0.010	2.5	"
4	0.004	0.010	0.26	0.014	0.010	0.045	0.0050	-	0.020	5.0	Comparison
5	0.005	0.024	0.11	0.017	0.007	0.048	0.0041	-	0.042	8.04	"
6	0.004	0.018	0.21	0.018	0.007	0.052	0.0053	0.075	-	8.06*	"
7	0.005	0.011	0.30	0.013	0.008	0.049	0.0047	0.025	-	2.58*	"
8	0.004	0.015	0.26	0.012	0.012	0.035	0.0070	0.022	0.030	6.0	"

\*  $Ti(\%) / [C(\%) + N(\%)]$

Sample steels listed in Table 1 were hot rolled to 4.0 mm thick at the finish hot rolling temperature of 910°C, treated at two levels, namely, coiling temperatures 720° and 620°C, respectively, then cold  
5 rolled to 0.8 mm thick, and thereafter subjected to the continuous anneal through the continuous anneal line with the annealing cycle as shown in Fig. 3. Namely, the steels were held at 800 - 850°C for a period of 30 seconds, and cooled to about 400°C at a cooling  
10 rate 5 - 100°C per second.

The results of quality test conducted on the cold rolled steel sheet thus obtained are shown in Table 2.

Tables 2-(1a) and 2-(1b) refer to the steels subjected to the coiling temperature 720°C while, Tables 2-(2a)  
15 and 2-(2b) to the steels treated at the coiling temperature 620°C.

Table 2-(1a)

Sample steel No.	Mechanical Property										Chemical treating ability	Re- marks
	Center in the longitudinal direction of coil											
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	EL (%)	YP-EL (%)	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>C</sub>	$\bar{r}$	Δr		
1	16.1	30.4	47.5	0.0	0.29	2.00	1.92	1.86	1.93	0.01	O	The inven- tion
2	16.4	31.0	48.1	0.0	0.30	1.94	2.00	1.85	1.95	-0.11	O	"
3	17.0	31.8	47.0	0.0	0.29	2.10	1.91	1.86	1.95	0.07	O	"
4	16.3	31.5	46.8	0.0	0.29	2.00	1.75	2.25	1.94	0.38	O	Com- pari- son
5	16.1	31.1	46.7	0.0	0.28	1.97	1.70	2.30	1.92	0.44	Δ-x	"
6	15.0	30.6	48.3	0.0	0.29	1.34	2.14	2.13	1.94	-0.41	x	"
7	18.0	32.2	46.5	0.2	0.26	1.85	1.15	2.05	1.55	0.80	O	"
8	17.0	32.5	45.0	0.0	0.28	1.97	2.07	1.75	1.97	-0.21	x	"

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Table 2-(1b)

Sample Steel No.	Mechanical Property										Chemical treating ability	Re- marks
	Average of leading and trailing portions of coil											
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	A.I.	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>C</sub>	r̄	Δr		
1	16.7	30.8	47.0	0.0	0.29	1.90	1.85	1.88	1.87	0.04	0	The inven- tion
2	16.6	31.8	47.5	0.0	0.28	1.83	1.98	1.84	1.91	-0.15	0	"
3	17.5	32.4	46.3	0.0	0.28	1.89	1.95	1.84	1.91	-0.09	0	"
4	23.5	35.1	38.6	0.0	0.24	1.60	1.34	1.83	1.53	0.38	0	Com- pari- son
5	24.0	35.3	38.1	0.0	0.23	1.50	1.30	1.89	1.50	0.40	Δ-x	"
6	15.2	30.6	48.2	0.0	0.28	1.31	2.10	2.13	1.91	-0.38	x	"
7	20.5	33.5	44.3	0.5	0.25	1.50	1.05	1.76	1.34	0.58	0	"
8	19.7	32.7	43.0	0.0	0.24	1.56	1.68	1.38	1.58	-0.21	x	"

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\* ) Test procedure and Evaluation

- 5 (1) Phosphate treatment consists of immersion  
type chemical of phosphophyllite,  $\text{Zn}_2\text{Fe}(\text{PO}_4)_2$ .  
GrS-D-2000 of Nippon Paint Co., Ltd. make  
was used; sample steel was immersed in a bath  
of adjusted TA16-18, AR18-20,  $\text{Zn}^{++}$   $1000 \pm 200$   
ppm,  $\text{Fe}^{++}$  50 - 100 ppm for a period of 120  
seconds. But the surface of the sample steel  
was polished by the grinder and used.
- 10 (2) Evaluation was conducted in the following  
manner: it was photographed by the scanning  
electron microscope to a photograph of 1000  
times as big, and the density and size of  
phosphate crystal were determined.
- 15 (O refers to good;  $\Delta$  to the one in which a  
part of steel sheet (less than 50%) was  
defective; and x refers to the one in which  
an area of more than 50% of the steel sheet  
was defective).
- 20

Table 2-(2a)

Sample Steel No.	Mechanical Property										Re-marks
	Center in the longitudinal direction of coil										
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	A.I.	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>C</sub>	$\bar{r}$	Δr	
1	16.5	30.8	47.0	0.01	0.28	1.90	1.86	1.87	1.87	0.03	The inven- tion
2	17.0	31.4	47.8	0.0	0.30	1.89	1.94	1.84	1.90	-0.08	
3	17.2	31.9	46.8	0.0	0.29	1.86	1.90	1.80	1.87	-0.07	
4	22.6	35.0	38.1	0.07	0.25	1.30	1.34	1.65	1.41	0.14	Com- pari- son
5	23.1	35.6	38.0	0.08	0.24	1.34	1.36	1.70	1.44	0.16	"
6	15.1	30.9	48.2	0.0	0.29	1.31	2.03	2.11	1.87	-0.32	"
7	21.0	34.0	44.0	0.4	0.23	1.40	1.05	1.62	1.28	0.46	"
8	19.5	32.4	44.0	0.0	0.24	1.60	1.72	1.42	1.62	-0.21	"

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Table 2-(2b)

Sample Steel No.	Mechanical Property										Re- marks
	Average of leading and trailing portions of coil										
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	YP-El (%)	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>C</sub>	$\bar{r}$	Δr	
1	16.6	30.9	46.8	0.01	0.29	1.89	1.85	1.88	1.87	0.07	The inven- tion
2	17.0	31.5	47.9	0.01	0.29	1.88	1.92	1.83	1.89	-0.07	
3	17.1	31.9	46.6	0.0	0.29	1.90	1.88	1.80	1.87	-0.03	
4	24.0	36.0	37.4	0.10	0.25	1.30	1.32	1.66	1.40	0.16	Com- pari- son
5	24.9	36.1	37.2	0.11	0.23	1.29	1.31	1.66	1.39	0.17	"
6	15.0	31.0	48.1	0.0	0.29	1.30	2.01	2.09	1.85	-0.31	"
7	20.7	33.7	44.0	0.6	0.23	1.42	1.02	1.65	1.28	0.52	"
8	20.8	33.1	43.2	0.0	0.24	1.58	1.60	1.28	1.52	-0.17	"

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Note:

$$(1) \text{ A.I. : Ageing Index A.I.} = \frac{\sigma_B - \sigma_A}{\sigma_A}$$

$\sigma_A$  : Stress at the time of tensile  
prestrain 7.5 - 8%

$\sigma_B$  : Yield strength when ageing 100°C x 1  
hour was treated after prestrain 7.5  
- 8%

$$(2) \bar{r} = \frac{1}{4}(r_L + 2r_{45^\circ} + r_C)$$

$$(3) \Delta r = \frac{1}{2}(r_L + r_C) - r_{45^\circ}$$



Fig. 4 shows the summary of distribution of mechanical properties in the longitudinal direction of the coil of sample steels. In Fig. 4, A refers to the steel containing Ti and Nb in combination sample steel 2; B to the Ti killed steel 6; C to the Nb  
5 killed steel 4; "a" to the coiling temperature 720°C; and "b" to the coiling temperature 620°C.

It is clear from Table 2 and Fig. 4 that the steel containing Ti and Nb of the invention has a distinguish-  
10 ed quality property as compared with the Ti or Nb killed steels of the prior art.

The Nb killed steel has a very high temperature of recrystallization at the usual coiling temperature of 620°C, consequently its yield strength is high while, on  
15 the contrary, its elongation is low. In the Nb killed steel subjected to the coiling temperature 720°C, its quality at the end portions of the coil is near the one of the usually coiled steel, because the cooling rate is large at the end portions of the coil. As a result, its  
20 yield is very low.

On the contrary, however, the Ti killed steel has a uniform excellent quality in the longitudinal direction of the coil, provided that Ti is sufficiently added to cause C and N to be precipitated. However, when the  
25 amount of Ti to be added is deficient in the precipitation of C and N, in other words, in case  $Ti/C + N$  (atomic ratio)  $< 1$  (7), its quality is exceedingly deteriorated.

On the other hand, however, the steel containing Ti and Nb together shows a uniform excellent quality, almost as same as that of the Ti killed steel containing an ample amount of Ti.

5 According to the test results of the secondary work cracking conducted on the sample steels with the drawing ratio of 3.0 as shown in Fig. 5, it has been clearly found that the Ti killed steel has the defect that the temperature range where cracking takes place is about 30°C higher than that of the Nb killed steel and also of the steel containing Ti and Nb together. Con-  
10 versely, the steel containing Ti and Nb together is on a good level as same as that of the Nb killed steel.

However, in case the cooling rate is so slow as  
15 in the box anneal, the temperature range where embrittlement occurs is raised on account of the segregation of P in the grain boundary in the course of cooling, hence it is required for the steel of the invention to be produced by the continuous anneal. In addition, the  
20 anisotropy of the  $r$  value should be particularly emphasized.

As shown in Fig. 4, in the steel coiled at the usual temperature,  $\Delta r$  of any steel is so relatively small, but in the steel coiled at the high temperature,  
25  $\Delta r$  of either Ti or Nb killed steel is considerably great.

Fig. 6 shows the typical interfacial anisotropy of  $\bar{r}$  value and  $r$  value of each steel; the  $r_L$  or  $r_{45^\circ}$  of the

Ti or Nb killed steels, respectively is very low, particularly, in the steel coiled at the high temperature, and it has a high possibility open to question at the time of subjecting to press forming of deep-drawing.

5 On the other hand, in the steel containing Ti and Nb together, the  $\bar{r}$  value of the steel coiled at the low temperature is not extremely low as the Nb killed steel, and the anisotropy is considerably small; and further, as compared with the  $r_L$  and  $r_C$ , the  $r_{45^\circ}$  is almost  
10 equal or a little large. It exhibits particularly an eminent formability in forming a square cylindrical body.

Fig. 7 shows the behavior of the  $r$  value where the reduction of cold rolling was varied. In Fig. 7, a refers to the coiling temperature  $720^\circ\text{C}$ , while b to the  
15 coiling temperature  $620^\circ\text{C}$ .

As described hereinbefore, the anisotropy of the  $r$  value of the steel containing Ti and Nb together is noticeably low as compared with that of either Ti or Nb killed steel, and this characteristic is clearly perceived whether the reduction of cold rolling is large  
20 or small. Moreover, the steel containing Ti and Nb together has a relatively high  $r$  value even with a low reduction of cold rolling. Thus, it is a good useful steel from the practical processing aspect.

25 As shown in Table 2, the steel containing Ti and Nb together has an eminent work hardness coefficient,  $n$  value, and is non-ageing as same as the Ti or Nb killed

steel.

According to the test results of chemical treating ability, it is seen that sample steels Nos. 5, 6 and 8 which exceed 0.04%(Nb + Ti) have inferior chemical treating ability, respectively. On the contrary, the steel of the invention has a good chemical treating ability.

Example 2

Table 3 shows the chemical composition of the steel of the invention and other steels for comparison.

Table 3

Sample Steel No.	Chemical Composition (wt%)										Chemical treating ability *2	Re- marks
	C	Si	Mn	P	S	Sol.Al	N	Ti	Nb	$\frac{Nb}{C}$		
8	0.004	0.025	0.15	0.065	0.004	0.047	0.0050	0.020	0.018	4.5	0	The inven- tion
9	0.003	0.210	0.17	0.071	0.007	0.054	0.0037	0.015	0.012	4.0	0	"
10	0.005	0.206	0.17	0.072	0.005	0.050	0.0051	--	0.020	4.0	0	Com- pari- son
11	0.005	0.180	0.16	0.070	0.007	0.040	0.0046	0.078	--	<sup>*1</sup> 8.13	x	"

\*1):  $Ti(\%) / [C(\%) + N(\%)]$ 

\*2): Test procedure and Evaluation are the same as Tables 2-(1a) and 2-(1b) and \*.

Sample steels listed in Table 3 including the steel containing Ti and Nb of the present invention, Ti killed steel and Nb killed steel of prior art, respectively, to which an alloying element has been added (chiefly, P) to make them high strength, respectively. The steels thus produced were hot rolled at the finish hot rolling temperature 910°C, coiled at 720°C to make them 4.00 mm, and then, they were cold rolled to 0.8 mm thick. Finally, they were annealed in the continuous anneal processing line with the anneal cycle shown in Fig. 3.

The test results of quality conducted on the above cold rolled steel sheet thus obtained are shown in Table 4.

Table 4

Sample Steel No.	Mechanical Property											Re- marks
	Center in the longitudinal direction of coil											
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	A.I.	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>C</sub>	$\bar{r}$	$\Delta r$		
8	19.1	38.8	41.2	0.0	0.27	1.73	1.89	1.70	1.80	-0.18	The inven- tion	
9	20.3	39.5	40.8	0.0	0.26	1.80	1.83	1.76	1.81	-0.05	"	
10	21.0	40.2	39.9	0.0	0.26	1.76	1.56	2.22	1.78	0.43	Com- pari- son	
11	18.8	38.5	41.0	0.0	0.26	0.91	1.84	1.85	1.61	-0.46	"	
Average of leading and trailing portions of coil												
8	19.4	39.3	40.5	0.0	0.26	1.76	1.86	1.70	1.80	-0.13	The inven- tion	
9	20.4	39.7	40.6	0.0	0.26	1.78	1.82	1.78	1.80	-0.04	"	
10	26.2	43.5	34.5	0.0	0.22	1.35	1.17	1.81	1.38	0.41	Com- pari- son	
11	19.0	38.9	40.5	0.0	0.25	0.99	1.83	1.75	1.60	-0.46	"	

Fig. 8 shows the distribution of quality characteristic values in the longitudinal direction of the coil of respective sample steels. In Fig. 8, the steel containing Ti and Nb refers to sample steels 8 and 9; the Ti killed steel to 11, and the Nb killed steel to 10. It is clear from Table 4 and Fig. 8 as follows: the Ti killed steel containing P has a disadvantage that the  $r$  value is inferior in the order of about 0.2 to the steel containing Ti and Nb together and the Nb killed steel in the center of the coil; the Ti killed steel containing P has a tendency to raise the temperature where secondary work cracking occurs as shown in Fig. 5. Further, in the Nb killed steel, the deterioration of quality in the end portion of the coil is noticeable.

As compared with the above steels of prior art, in the steel containing Ti and Nb, the level of the  $r$  value is equally high in the center of the longitudinal direction of the coil as same as the Nb killed steel, and the distribution of quality in the longitudinal direction of the coil is extremely uniform as same as the Ti killed steel.

In addition, the anisotropy of the  $r$  value of the steel of the invention is extremely small, which is a distinguished characteristic unobtainable in both Ti killed and Nb killed steels. Thus, it is clear that the steel of the invention has a distinguished superiority to



any steel made high strength by adding an alloying element.

Example 3

Sample steels 2, 3, 5, 6, 8, 10 and 11 selected  
5 from those listed in Tables 1 and 3 were cold rolled  
under the same conditions as described in Example 2,  
and thereafter the molten zinc coated steel sheet was  
produced from them, respectively, with the anneal cycle  
as shown in Fig. 9 wherein the steels were held at a  
10 temperature of 800 - 850°C for a period of 30 seconds;  
(a) cooled to about 450°C with a cooling rate of 3° -  
100°C/sec.; (b) treated in the molten zinc bath of  
450° - 500°C; and (E) subjected to an alloying treat-  
ment (d) at about 500° - 560°C. The cycle (F) refers to  
15 the case where the alloying treatment was not carried  
out while (E) to the case where the alloying treatment  
was carried out to produce the alloyed zinc coated steel  
sheet. The mechanical properties of the zinc coated  
steel sheet were hardly affected by the operation whether  
20 the alloying treatment was carried out or not. Tables 5a, 5b  
show the quality characteristic value of the zinc coat-  
ed steel sheet wherein the alloying treatment (E) was  
carried out.

Table 5a

Sample Steel No.	Mechanical Property										Re- marks
	Center in the longitudinal direction of coil										
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	A.I.	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>c</sub>	$\bar{r}$	$\Delta r$	
2	16.9	31.4	47.9	0.0	0.30	1.99	1.91	1.85	1.92	0.01	The inven- tion
3	17.1	32.0	46.6	0.0	0.29	2.05	1.89	1.87	1.93	0.07	"
5	16.7	31.7	46.3	0.0	0.28	1.94	1.67	2.36	1.91	0.48	Com- pari- son
6	15.3	30.7	47.9	0.0	0.29	1.30	2.11	2.09	1.90	-0.42	"
8	19.5	39.1	40.7	0.0	0.27	1.70	1.88	1.71	1.79	-0.18	The inven- tion
10	21.5	40.6	39.8	0.0	0.26	1.73	1.52	2.17	1.74	0.43	Com- pari- son
11	18.7	38.4	40.5	0.0	0.26	0.88	1.80	1.81	1.57	-0.46	"

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Table 5b

Sample Steel No.	Mechanical Property										Re- marks
	Average of leading and trailing portions of coil										
	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	A.I.	n	r <sub>L</sub>	r <sub>45°</sub>	r <sub>C</sub>	$\bar{r}$	$\Delta r$	
2	16.9	31.5	46.9	0.0	0.29	1.90	1.85	1.88	1.87	0.04	The inven- tion
3	17.8	32.7	46.0	0.0	0.27	1.87	1.93	1.82	1.89	-0.09	"
5	24.9	35.8	37.6	0.10	0.23	1.46	1.36	1.86	1.51	0.30	Com- pari- son
6	15.6	30.8	48.1	0.0	0.28	1.28	2.07	2.11	1.88	0.38	"
8	19.7	39.8	40.3	0.0	0.26	1.75	1.88	1.69	1.80	0.03	The inven- tion
10	26.6	44.0	34.0	0.11	0.21	1.31	1.13	1.75	1.33	0.40	Com- pari- son
11	19.1	39.0	40.3	0.0	0.24	0.96	1.79	1.71	1.56	-0.38	"

The quality and characteristic properties of each sample steel show almost the same tendency as those obtained in Examples 1 and 2. Therefore the steel of the invention is extremely excellent as a molten zinc coated steel sheet. In the steel sheet coated with the alloyed zinc coating layer, if the alloying reaction proceeds too excessively, a brittle alloyed layer grows so much that there arises a danger which causes powdering when the coated sheet is subjected to the press forming work.

Table 6 shows the test results of powdering in which 10 coils were produced from each steel, 10 samples were taken from them, namely, 100 samples in all were collected from them, and the powdering test was conducted on each sample.

Table 6

Sample Steel	2	3	5	6	8	10	11
Rate of Occurrence of Powdering	2%	2%	1%	31%	1%	0%	22%
	$(\frac{2}{100})$	$(\frac{2}{100})$	$(\frac{1}{100})$	$(\frac{31}{100})$	$(\frac{1}{100})$	$(\frac{0}{100})$	$(\frac{22}{100})$
Remarks	The invention	"	Comparison	"	The invention	Comparison	"

In the Ti killed steel, the rate of occurrence of powdering is very high, because Ti promotes the alloying reaction of iron base with molten zinc to accelerate a

super-alloying reaction. The steel containing Ti and Nb of this invention is almost on the same level as the Nb killed steel, and has a very good resistance to powdering. In this respect, the steel of the invention is a most suitable stock for a good alloyed zinc coated steel sheet.

#### Example 4

A steel slab having the chemical composition shown in Table 7 was produced, and the slab was hot rolled under the hot rolling requirement indicated in Table 8. The finish hot rolling temperature was in the range of 890 - 910°C, respectively. A hot rolled steel sheet was 3.8 mm thick, then after pickling it was cold rolled to 0.8 mm thick, and thereafter the cold rolled steel sheet was annealed in a continuous anneal furnace. The anneal cycle was about 10°C/sec., the steel was heated to 780° - 820°C, held at said temperature range for a period of 40 seconds, and then cooled to the room temperature at an average cooling rate 50 - 100°C/sec. The steel was subjected to the 0.8% skin pass rolling, and thereafter the quality test was conducted on every steel sheet. The test results including the chemical treating ability and secondary work cracking are shown in Table 8.

The steel of the present invention (refers to Nos. 1 - 3) shows good results, respectively. To sample steel No. 4 no B was added, so the secondary work cracking tends to occur while, conversely, to No. 5 too much B was added,

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hence the values of  $Y_P$ ,  $E_L$ , and  $r$  were not satisfactory, respectively.

Table 7

Sample Steel No.	Chemical Composition (wt.%)										Hot Rolling Requirement	
	C (ppm)	Si	Mn	P	S	Al	N (ppm)	B (ppm)	Nb	Ti	Heat. Temp. (°C)	Coil. Temp. (°C)
1	31	0.01	0.15	0.015	0.01	0.050	36	3	0.015	0.005	1250	680
2	48	0.01	0.18	0.010	0.01	0.045	40	15	0.020	0.018	1200	700
3	48	0.02	0.17	0.017	0.01	0.041	47	10	0.020	0.014	1210	710
4	40	0.01	0.16	0.011	0.01	0.048	38	-	0.015	0.015	1250	680
5	41	0.01	0.15	0.014	0.02	0.045	35	37	0.016	0.012	1250	680

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Table 8

Sample Steel No.	YP (Kgf/mm <sup>2</sup> )	TS (Kgf/mm <sup>2</sup> )	El (%)	$\bar{r}$ value	n value	Yield point elongation (%) (after ageing 100°C x 1 hr.)	Secondary workability	Chemical treating ability**
1	15.7	31.5	50.0	2.10	0.25	0.0	3.9	0
2	15.0	30.5	52.1	2.20	0.27	0.0	3.9	0
3	15.2	30.7	52.2	2.28	0.27	0.0	3.9	0
4	16.2	31.8	50.0	2.00	0.25	0.0	2.5	0
5	18.5	33.1	47.5	1.76	0.24	0.0	3.7	0

Note: \* : Cracking test was conducted at -70°C. Deformation rate 200 mm/min. Values were shown as the largest drawing ratio where no cracking occurred.

\*\* : Test procedure and evaluation are the same as shown in Table 2-(1a) and Table 2-(1b).

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Example 5

Sample steels containing the very low carbon content listed in Table 9 were subjected to the continuous casting process to make a slab casting process, respectively. To sample steel No. 7 only Nb and to No. 6 only Ti was added. Steels Nos. 6 - 7 were for comparison. In hot rolling, the surface heating temperature was 1150°C, its finish temperature in the range of 740°C - 860°C, and the steel was coiled at 650°C. The hot rolled steel sheet 3.2 mm thick was pickled, then cold rolled to the cold rolled sheet 0.8 mm thick, and thereafter subjected to the recrystallization anneal in the continuous anneal furnace at 830°C for a period of 35 seconds. The 0.8% skin pass rolling was conducted on the steel sheet, and thereafter the quality and chemical treating ability thereof were determined to obtain the test results as shown in Table 10.

Comparative steel No. 5 contained Nb + Ti = 0.048 wt% to show its inferior result in the chemical treating ability; and its Nb content was too high, so its yield point was high and its elongation was low. Comparative steel No. 6 contained Ti in an amount of less than the equivalent of (C + N), and it was deficient in ductility and somewhat hard, and the r value was unsatisfactory; particularly, the r value in the 45° direction was deficient. Comparative steel No. 7 contained only

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Nb, and it was found that the r value was sufficiently high while, on the other hand, its ductility was inferior and hard; and the satisfactory quality was not attained by the low temperature coiling process.

Table 9

Sample Steel No.	Chemical Composition (wt %)									Slab Heating Temp. (°C)	Finish Temp. (°C)	Coil- ing Temp. (°C)
	C	Si	Mn	P	S	Sol.Al	N	Ti	Nb			
1	0.0030	0.019	0.23	0.012	0.010	0.035	0.0025	0.012	0.007	1150	740	650
2	0.0040	0.02	0.18	0.013	0.005	0.045	0.0035	0.010	0.015	1150	860	650
3	0.0025	0.032	0.15	0.015	0.006	0.058	0.0052	0.013	0.010	1150	800	650
4	0.005	0.030	0.25	0.018	0.005	0.042	0.0042	0.014	0.022	1150	780	650
5	0.004	0.02	0.28	0.017	0.007	0.048	0.0047	0.020	0.028	1150	860	650
6	0.003	0.05	0.21	0.015	0.008	0.048	0.0052	0.025	-	1150	840	650
7	0.003	0.02	0.17	0.014	0.008	0.055	0.0035	-	0.020	1150	840	650

Table 10

Sample Steel No.	YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	r value	YP-El (%) after ageing 100°C x 1 hr.	Chemical Treating Ability*	Remarks
1	17	32	47	1.83	0	0	The invention
2	17	32	48	1.95	0	0	"
3	18	32	48	1.85	0	0	"
4	18	32	46	1.89	0	0	"
5	20	33	44	1.75	0	Δ	Comparison
6	21	33	42	1.50	0.5	0	"
7	22	34	42	1.72	0.2	0	"

Note: \* Test Procedure and Evaluation are the same as shown in Table 2-(1a) and Table 2-(1b).

Example 6

Steel having the composition consisting of 0.003%C, 0.025%Si, 0.23%Mn, 0.015%P, 0.008%S, 0.045%sol-Al, 0.0045%N, 0.012%Ti and 0.012%Nb (percentage being by weight) was subjected to the continuous casting process to produce many slabs; and these slabs were subjected to the hot rolling at the slab heating temperature and at the finish hot rolling temperature as shown in Table 11 to produce the hot rolled coil 3.0 mm thick, and finally the coil was obtained at a temperature in the range of 620 - 650°C by coiling itself.

After pickling, the coil was cold rolled to produce a cold rolled steel sheet 0.8 mm thick, and then the steel sheet was annealed in the continuous anneal process at 780°C for a period of 35 seconds in order to do the recrystallization anneal. After the 0.8% skin pass rolling, its quality and chemical treating ability were determined to obtain the results as shown in Table 11.

In sample steels Nos. 6 and 7 wherein the finish hot rolling was completed at 910°C, (Nb·Ti)C was not fully precipitated in the hot rolled sheet so that it was hard and had an inferior ductility, and the r value was not satisfactory. Sample steel No. 5 had a somewhat inferior quality on account of the high heating temperature. As regards sample steels Nos. 1-4, their slabs were heated at a low temperature, hence the useful effect of the present invention exhibited so sufficiently that the distinguished results were obtained.

Table 11

Sample Steel No.	Slab Surface Heat. Temp. (°C)	Finish Temp. (°C)	PROPERTY					Chemical Treating Ability *
			YP (Kg/mm <sup>2</sup> )	TS (Kg/mm <sup>2</sup> )	El (%)	r value	YP - El (%) after aging 100°C x 1 hr	
1	1050	720	15	31	50	1.9	0	0
2	"	800	15	31	51	2.1	0	0
3	"	850	15	31	51	2.1	0	0
4	980	800	14	30	52	2.2	0	0
5	1250	800	18	33	46	1.78	0.1	0
6	1250	910	20	33	45	1.70	0.2	0
7	1150	910	19	33	46	1.77	0.1	0

Note: \* Test Procedure and Evaluation are the same as shown in Tables 2-(1a) and 2-(1b).

## WHAT IS CLAIMED IS:

1. Method for the production of cold rolled steel sheets having super deep drawability characterized by the steps of providing a steel containing, in weight %, less than 0.007%C, less than 0.8%Si, less than 1.0%Mn, less than 0.1%P, 0.01 - 0.1%Al, less than 80 ppm N, Ti in an amount of the specified range:  $48/14(N\% - 0.002\%) < Ti\%$  and  $Ti\% < (4.00C\% + 3.43N\%)$ , Nb in an amount of the specified range:  $Nb\% > 2.33C\%$  and more than 0.003% to less than 0.025%,  $Nb + Ti < 0.04\%$ , the remainder Fe, and unavoidable impurities, hot rolling said steel, cold rolling said hot rolled steel, and finally, subjecting said cold rolled steel to a continuous anneal at a temperature of more than 700°C to less than the  $Ac_3$  transformation point.
2. Method as claimed in Claim 1 in which the total amount of Nb and Ti is in the range of  $0.01\% < Nb\% + Ti\% < 0.04\%$ .
3. Method as claimed in Claims 1 and 2 in which said steel contains less than 30 ppm B.
4. Method as claimed in Claim 3 in which said steel contains 2 ppm - 10 ppm B.
5. Method as claimed in Claims 1 to 4 in which said steel is subjected to the finish hot rolling at a

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temperature of 720°C - 870°C, and said hot rolled steel sheet is coiled at a temperature of less than 680°C.

6. Method as claimed in Claim 5 in which the heating temperature of a slab obtained from said steel before said hot rolling is in the range of 950 - 1170°C.



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FIG. 1

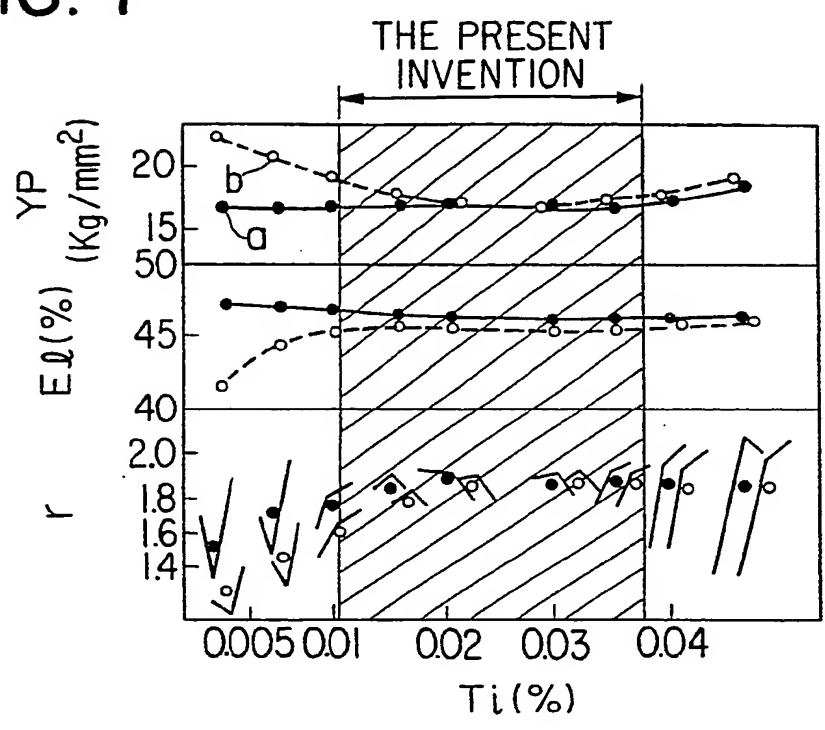
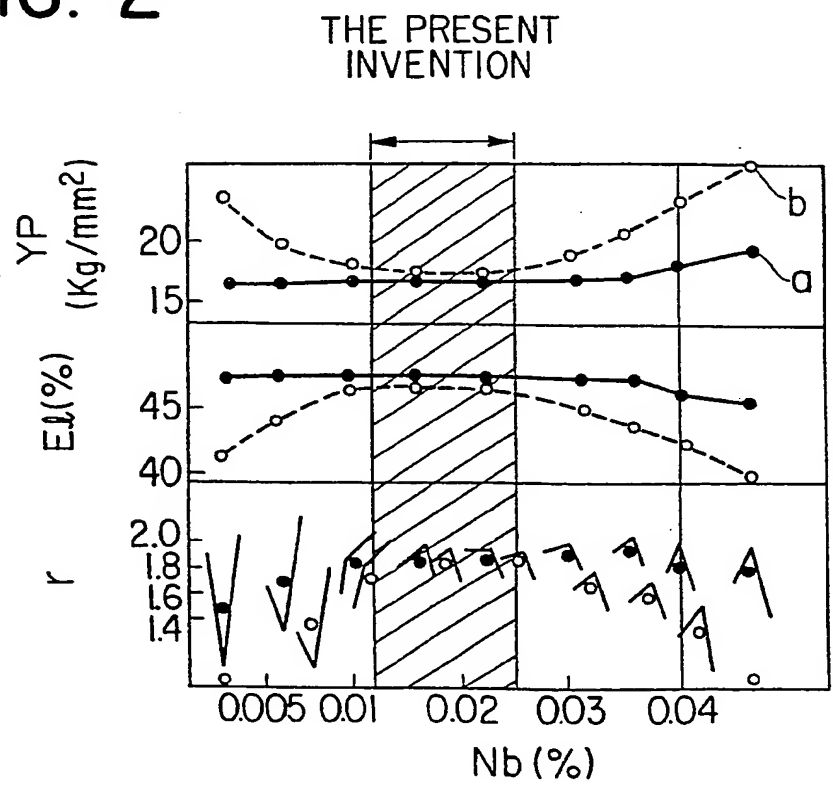


FIG. 2



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FIG. 3

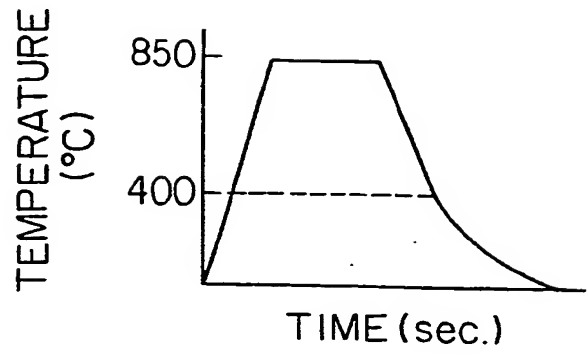
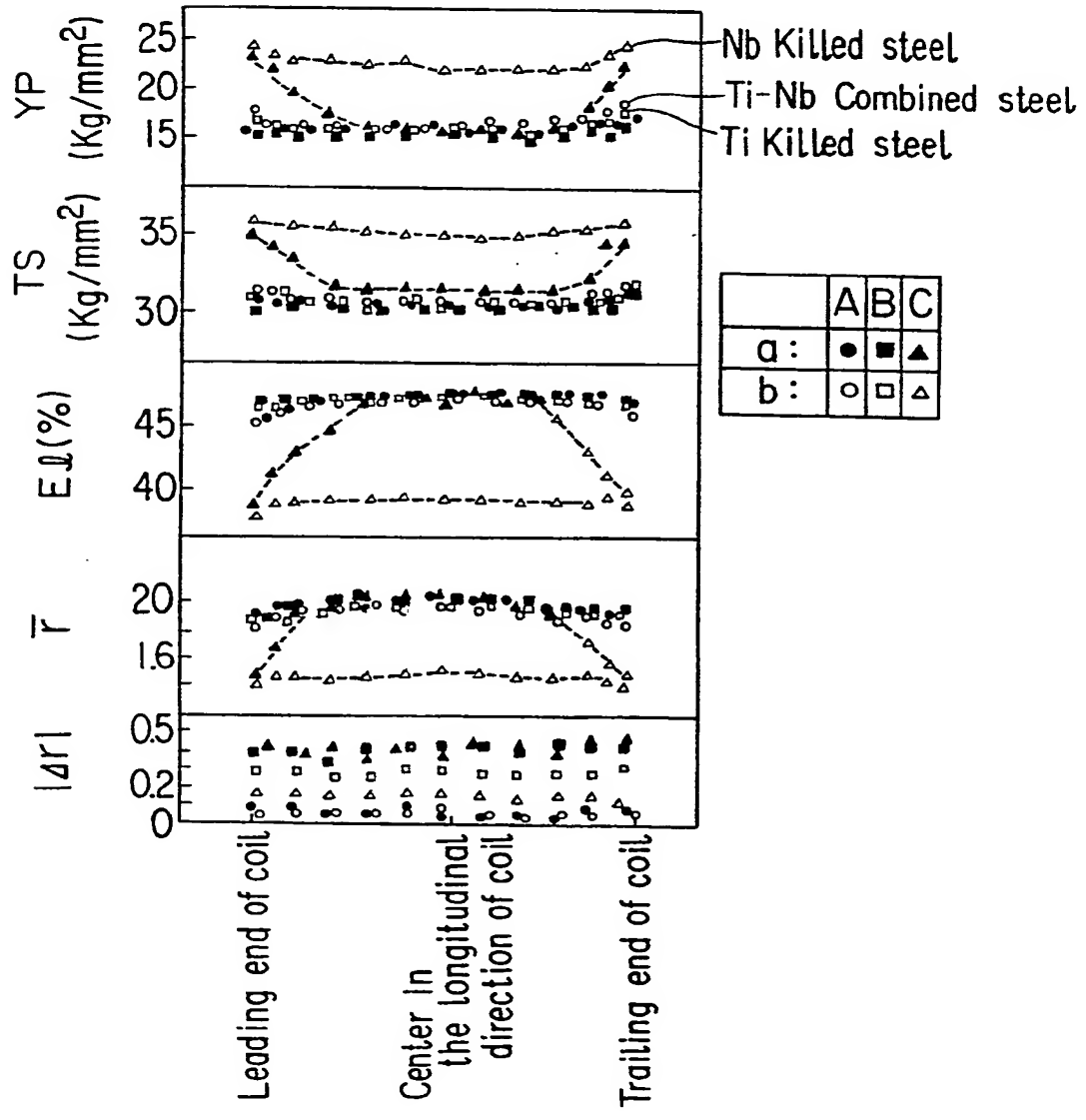


FIG. 4



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FIG. 5

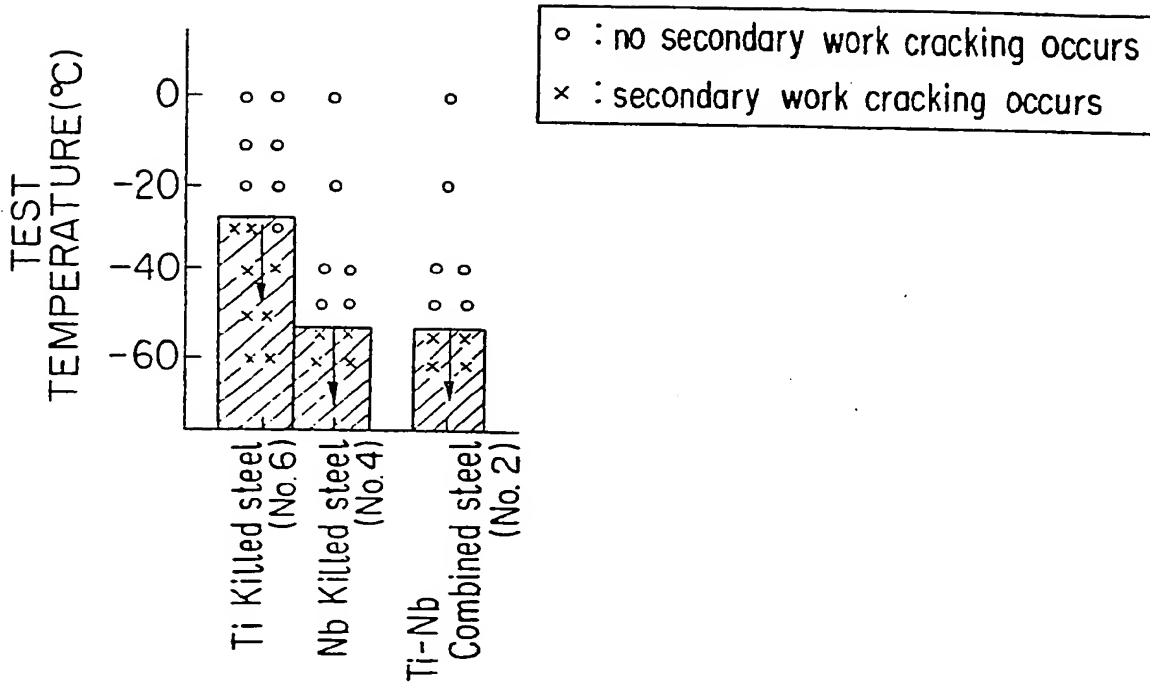
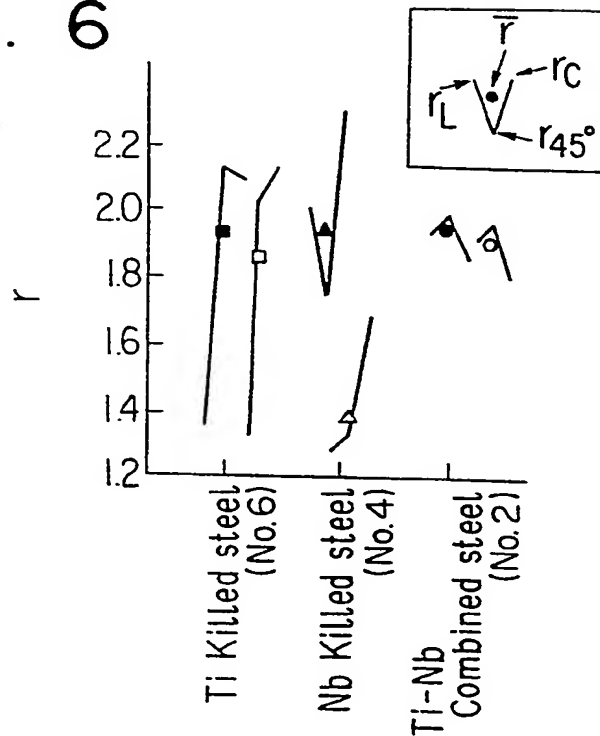


FIG. 6



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FIG. 7

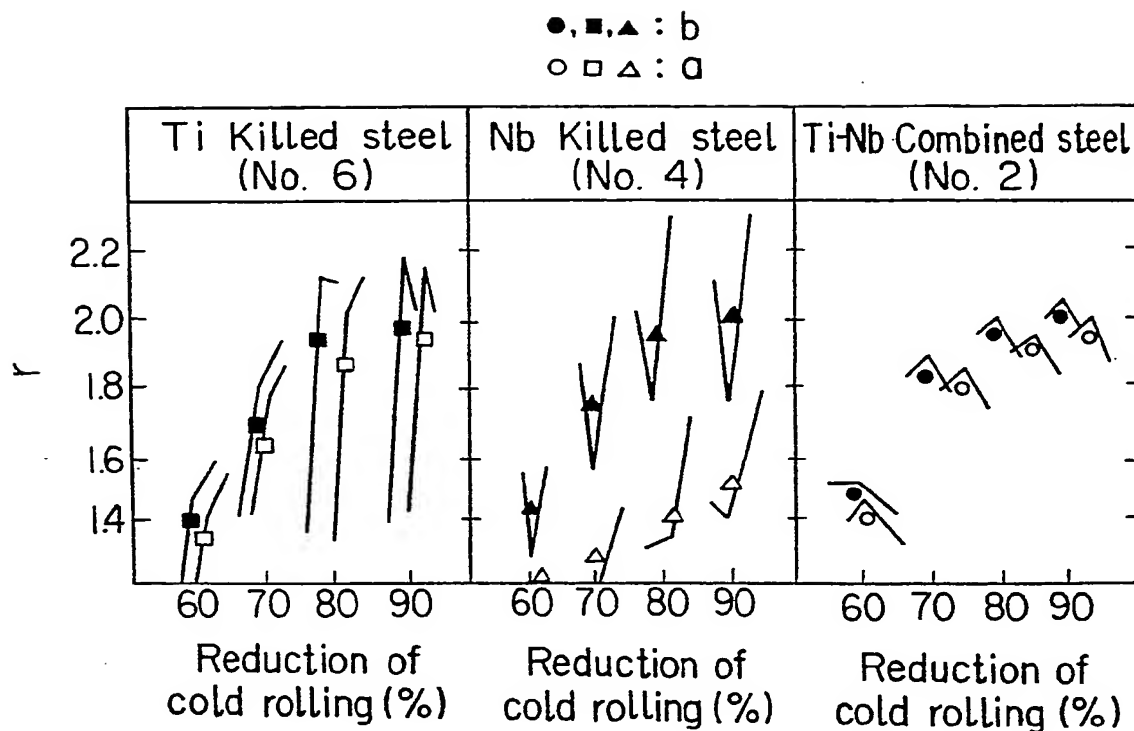
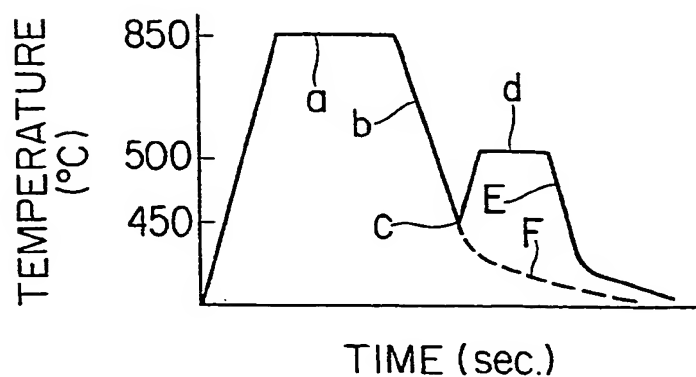
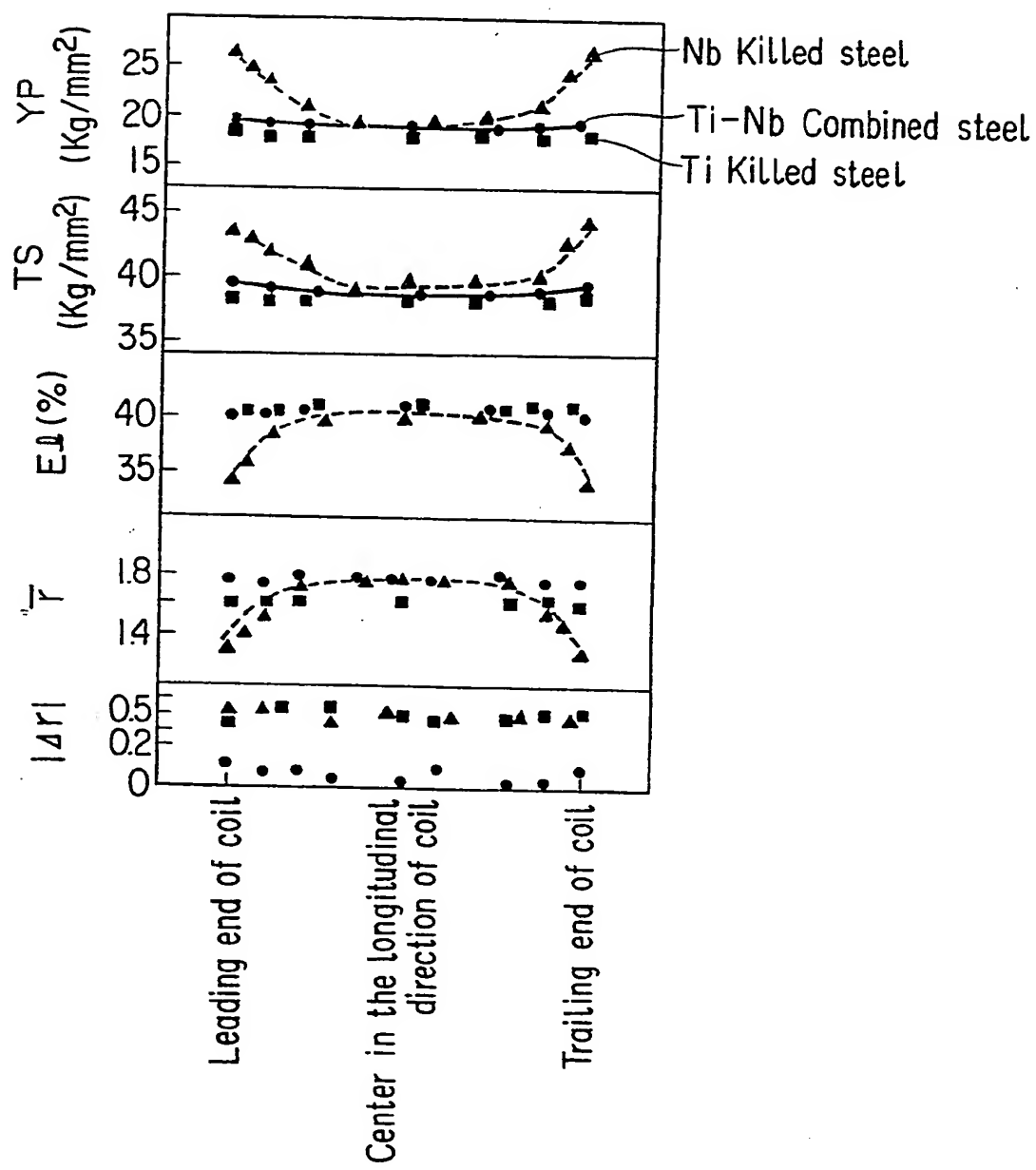


FIG. 9



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FIG. 8





European Patent  
Office

# EUROPEAN SEARCH REPORT

0108268

Application number

EP 83 11 0039

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 2)
Y,D	US-A-3 765 874 (ELIAS et al.) * Abstract; claims ---	1-3,5 6	C 21 D 8/04 C 21 D 9/48 C 22 C 38/12
Y	EP-A-0 048 351 (NIPPON STEEL) * Claims * ---	1-3,5 6	
Y	DE-A-2 362 658 (NIPPON STEEL) * Claims; page 11, lines D-N; page 9, paragraph 3 - page 10, paragraph 1 * ---	1-3,5 6	
A	US-A-4 125 416 (NIPPON STEEL) ---		
A	WO-A-8 201 893 (KAWASAKI) & EP - A - 0 067 878 (Cat. P,A) ---		TECHNICAL FIELDS SEARCHED (Int. Cl. 2)
A,D	US-A-3 522 110 (SHIMIZU et al.) ---		C 21 D C 22 C
A	DE-A-2 247 690 (KAWASAKI) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31-01-1984	Examiner OBERWALLENEY R.P.L.I
CATEGORY OF CITED DOCUMENTS			
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